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Passive sampling for monitoring polar organic pollutants in water by three typical samplers

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ABSTRACT

Passive sampling technique is an important supplementary tool in pollution monitoring. In recent years, samplers designed for the hydrophilic organic pollutants, including polar organic chemical integrative sampler (POCIS), Chemcatcher®, and diffusive gradients in thin film technology (DGT), have been successfully applied in both laboratory experiments and field studies. This review gives an overview of the application of these passive samplers for monitoring the polar organic pollutants. Sampler structures, material compositions, and the calculation of time weighted average concentrations were also compared. Besides, difference of the three samplers on the scope of the target analytes and exposure time, as well as the effects of environmental factors, e.g. hydrodynamic conditions, temperature, pH, ionic strength, DOM, on sampling performance were also introduced.

1. Introduction

Water is an important source and sink of polar (hydrophilic) organic compounds, which are unlikely to adsorb on the soils and sediments due to their low log K_{ow} (octanol-water partition coefficient) values. For example, a majority of herbicides and pesticides are with good water solubility to facilitate the use of farmers [1], which are prone to releasing to water through leaching and runoff [2,3]. In addition, the discharge of the wastewater treatment plants (WWTPs) to surface water also contains many polar organic chemicals, such as antibiotics, pharmaceuticals [4,5], some of which are hard to be biodegraded [3].

As many micropollutants have been detected at trace levels in the water environments [6], it is essential to monitor their environmental occurrence. Although traditional grab sampling is low-cost and simple, there are some limitations on this method. For example, a large volume of water sample need to be concentrated for trace contaminants, and the sample preparation protocols are usually tedious. Besides, the instantaneous concentration obtained by this method is unrepresentative, especially for the instantaneous peak of the contaminants.

Passive sampling is emerging as a popular water monitoring method for the detection of both inorganic and organic pollutants [7–9], as well as nanoparticles [10], where the amounts of chemicals were accumulated over time and time weighted average concentrations (TWACs) were determined to reveal the real exposure level. In addition, passive sampling can realize the preconcentration to simplify the pretreatment process. Passive samplers were initially accepted to imitate the lipophilic bioaccumulation of chemicals in the water and sediments [11–13]. Gradually, several passive sampling devices, such as Chemcatcher®, polar organic chemical integrative sampler (POCIS), have been developed for monitoring polar organic group of contaminants [14–16]. In recent years, diffusive gradients in thin film technology (DGT) which are initially designed for the accumulation of metals are proved to be suitable for polar organic compounds with some modifications in binding gels [17,18].

Recently, more molecules were monitored by the passive sampling technologies, and the influences of environmental factors on sampling rate (R_s) were further studied. Moreover, some new materials, like molecularly imprinted polymer (MIP), ionic liquids, are used as the receiving phase in passive samplers to promote the sampling selectivity. In current review, the configuration, performance and application of three typical passive samplers, Chemcatcher®, POCIS, and DGT are introduced, and the limitation and the development of polar organic pollutants passive sampling is prospected.

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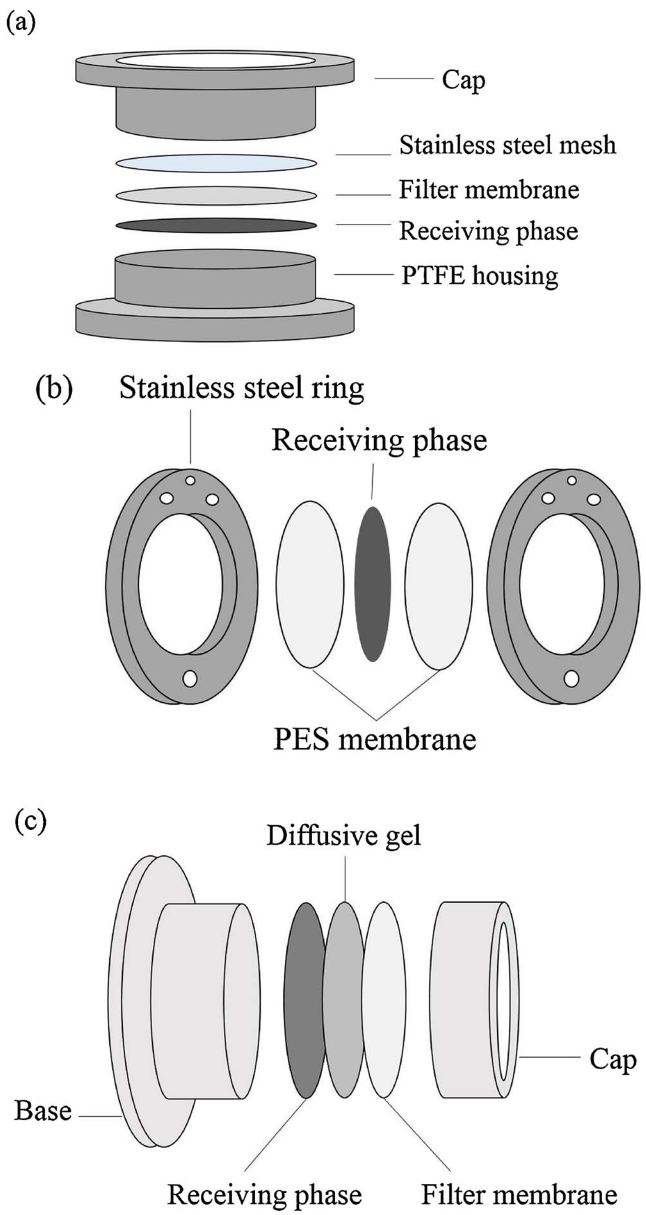

Fig 1. The configuration of Chemcatcher (a), POCIS (b), and DGT (c) [17,20,105].

2. Commercial passive samplers and their configuration

2.1. Chemcatcher®

Chemcatcher® has been deployed for accumulating organic pollutants in aquatic environment about 15 years, and it consists of a disk as receiving phase with or without a limiting diffusion membrane sealed into a polycarbonate (PC) or polytetrafluoroethylene (PTFE) housing (Fig. 1(a)) [19]. The prototype designed to subsequent polar organic pollutants has a C_{18} disk as receiving phase and polysulfone (PS) membrane as rate-limiting membrane [20]. With the development of passive sampler, several SPE disks, which are broad-spectrum extraction material without specificity, and polymer films have been adopted for Chemcatcher®. And the depth of the cavity where the disk and prefilter membrane are located inside is reduced from 20 mm to about 2 mm. This results in a thinner water boundary layer and the increased sampling rate.

One of the greatest strengths of Chemcatcher® is its good performance on sampling various contaminants by the use of a proper combination of receiving phase and membrane. For instance, C_{18} covered with an low-density polyethylene (LDPE) membrane is the most commonly used receiving phase for hydrophobic compounds [21–23], while chelating disk associated to cellulose acetate (CA) membrane is suitable for trace metals [24,25], as well as rare earth elements [26].

2.2. POCIS

POCIS is a passive sampling technology developed for in-situ collecting time-weighted average exposures to the hydrophilic organic contaminants with log K_{ow} less than 3, which includes most pharmaceuticals, illicit drugs, polar pesticides, phosphate flame retardants, surfactants, metabolites and degradation products [27].

Two configurations of the POCIS, i.e. pesticide-POCIS and pharmaceutical-POCIS, are present as the commercial products. Both two kinds of the POCISs consist of an array of sampling disks mounted on a support rod. Each disk consists of a solid sorbent sandwiched between two polyethersoulfone (PES) microporous membranes which are then compressed between two stainless steel rings, and its configuration are shown in Fig. 1(b). Because the PES membranes are not able to be heat sealed, stainless steel rings or other rigid inert material are applied to prevent loss of sorbent from the samplers. The difference in pesticide-POCIS and pharmaceutical-POCIS is the solid sorbent. A standard POCIS disk consists of a sampling surface area to sorbent mass ratio of approximately 180 cm^2/g.

2.3. DGT

DGT was firstly developed by Davlson and Zhang in 1994 [28], which was originally designed for in-situ detecting trace metals and labile inorganic chemicals in aquatic environments and soil systems [29–31]. In recent years, the scope of application is extended to organic contaminants, while the first o-DGT (for organic pollutants) was proposed in 2012 [17], with some modifications on DGT configuration [18,32,33].

From the surface to the internal, DGT is generally composed of a protected prefilter, diffusive hydrogel and binding agent (Fig. 1(c)). The greatest advantage of DGT over other passive samplers like POCIS and Chemcatcher®, is that quantitative analysis of field deployment needs no calibration, as R_s of DGT is independent on hydrodynamic conditions.

3. Functional materials of the samplers

3.1. Receiving phases

3.1.1. Chemcatcher®

For polar organic compounds (log K_{ow} less than 4), there are three main types of receiving phases applied in Chemcatcher®, i.e. SDB-RPS (styrenedivinylbenzene-reverse phase sulfonated), SDB-XC (styrenedivinylbenzene-exchange) and C_{18} disk (Table 1). Both SDB-RPS and SDB-XC disks are poly (styrenedivinylbenzene) copolymers, whereas the modification with sulfonic acid groups on the former sorbents increases the hydrophilicity and the latter containing no polar or ionizable functional groups is hydrophobic. As a result, SDB-RPS disk can retain ionizable and polar analytes through the mechanisms including π-π bonding [34], hydrogen bonding, as well as van der Waals and Coulomb interactions [35]. Kaserzon et al. [35] showed that SDB-XC disk can be used for sampling polar organic contaminants like carbamazepine, but not ionizable ones. Furthermore, the combination of HLB sorbents and Chemcatcher® sampler are carried out by Bruce et al. for the detection of pharmaceuticals, personal care products, and illicit drugs, which provides the suitability for polar chemicals by HLB sorbents as well as the handling benefits, compared to POCIS [36]. C_{18} is a silica sorbent bonding with octadecyl groups to make it hydrophobic. The "naked" (without limiting diffusion membranes) Chemcatcher® sampler with a C_{18} disk are more prone to adsorbing and sequestering